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PENTAMOLYBDOBIS (CIS-PHOSPHATOBISETHYLENEDIAMINEAQUOCOBLT(III))--ETC(U)
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N00014-75-C-0945

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Task No. NR 053-576

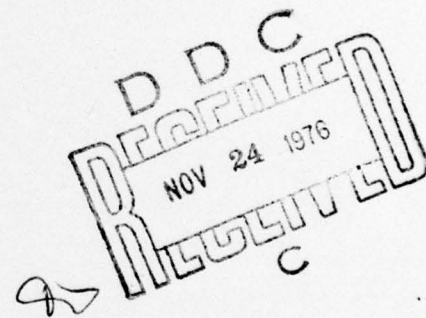
Technical Report No.5

Pentamolybdo-bis[cis-phosphatobisethylenediamineaquocobalt(III)].
A 'Neutral' Heteropoly Complex

by

Wonsuk Kwak and Michael T. Pope
Department of Chemistry, Georgetown University
Washington, D.C.

Prepared for Publication
in
Inorganic Chemistry



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Pentamolybdois[*cis*-phosphatobisethylenediamineaquacobalt(III)].

A 'Neutral' Heteropoly Complex

Wonsuk Kwak and Michael T. Pope

We have recently reported some of the first examples of organic derivatives of heteropoly anions^{1,2}. Among the new complexes were pentamolybdoisphosphonates, (RP)₂Mo₅O₁₁³⁻, that are structurally analogous³ to the corresponding molybdophosphate⁴, (OP)₂Mo₅O₁₁³⁻. In these heteropoly complexes the heteroatom, phosphorus, utilizes only three oxygens to bind to the oxometallate structure. The pentamolybdoisphosphonate anions form rapidly and are hydrolytically stable at pH 4-5. Under these conditions, complexes where R contains an amino group are protonated, and the resulting heteropoly anions are zwitterionic, e.g. [(H₃N⁺C₂H₄P)₂Mo₅O₁₁]¹⁻. In this paper we describe the synthesis of an electrically neutral zwitterion of the same type in which the hetero group is a monodentate phosphate ligand of an inert coordination complex.

Experimental

The complexes *cis*-[Co(en)₂(H₂O)(HPO₄)]ClO₄·0.256H₂O, [Co(en)₂PO₄]₂·H₂O and *cis*-[Co(en)₂(H₂O)₂](NO₃)₂ were prepared as previously described^{5,6}. The last named complex was converted to the perchlorate salt by treatment with sodium perchlorate. Optical spectra of these complexes agreed with those reported^{5,7}. Preparation of [Co₂(en)₃(H₂O)₂P₂Mo₅O₁₁]₂·8H₂O. The complex *cis*-[Co(en)₂(H₂O)(HPO₄)]⁺ was prepared by dissolving 0.56 g of

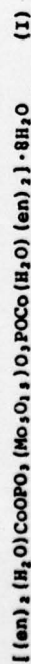
[Co(en)₂PO₄]₂·H₂O (2 mmol) in 100 ml of water and adjusting the pH to 4.7 with dilute sulfuric acid⁵. A solution containing 1.45 g of Na₂MoO₄·2H₂O (6 mmol) in 20 ml water was adjusted to pH 4.4 with dilute sulfuric acid. Both solutions were separately filtered to remove dust and the filtrates chilled to 10-15° in an ice-bath. The molybdate solution was added dropwise to the cobalt solution, keeping the pH of the mixture at 4.4-4.7 by the addition of sulfuric acid, and keeping the temperature at 10-15°. A brick red precipitate began to form when ca 2 ml of the molybdate solution had been added. After the final addition of the molybdate solution, the suspension was kept in a refrigerator for two hours. The precipitate was collected by filtration, washed successively with a large amount of water acidified to pH 4.5, and acetone, and air-dried. The dried product was red-violet and weighed 1.1 g. Anal. Calcd. for Co₂C₆N₆H₁₂P₂Mo₅O₁₁·2H₂O: C, 6.64; H, 3.62; N, 7.73; P, 4.28; Mo, 33.12; H₂O, 9.95. Found⁸: C, 6.69; H, 3.63; N, 7.82; P, 4.41; Mo, 33.14; H₂O (wt. loss 110-115°), 11.26.

Results and Discussion

The complex is insoluble in water at pH 3-5, and in common polar and non-polar solvents (alcohols, dimethylsulfoxide, dimethylformamide, propylene carbonate, acetonitrile, nitromethane, benzene, etc.). At pH 6 or above the complex dissolves to give a clear solution of [Co(en)₂PO₄] (maximum at 529 nm) and, presumably, MoO₄²⁻ ions. If this solution is reacidified to pH ca 4, the heteropoly complex is reformed.

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The analytical data support the formulation as a neutral zwitterion (or alternatively as a binuclear cobalt complex):



The infrared spectrum of the complex in the metal-oxygen stretching region is shown in Figure 1 together with that of sodium pentamolybdo-diphosphate, and is characteristic² of the P_2Mo_2 moiety. Optical absorption data are given in Table 1. Energies of the first d-d bands are generally reliable indicators of the constitution of the first coordination sphere of the cobalt(III) ion^{9,10,11}. The data in Table 1 thus support formula I with $[\text{CoN}_6(\text{aq}) (\text{monodentate phosphate})]$ rather than a salt such as $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]_2[\text{P}_2\text{Mo}_2\text{O}_{12}]$. The salt formulation is also ruled out by the hydrolytic dissolution of the complex at pH 6 to give $[\text{Co}(\text{en})_2(\text{PO}_4)]$.

We conclude that the complex formed is indeed a neutral zwitter-ionic species. The interconversion of $[\text{Co}(\text{en})_2(\text{PO}_4)]$ to $\text{cis}[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OPO}_3\text{H})]^+$ in aqueous solution occurs rapidly at pH 5⁵, and polymerization of molybdate is also rapid under these conditions. The resulting structure offers a number possibilities for isomerism, since both the $\text{cis}[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{O}-)]$ and $\text{P}_2\text{Mo}_2\text{O}_{12}$ moieties are chiral. It is mildly surprising, and somewhat disappointing, that the resulting zwitterion is insoluble. We presume that the approximately linear charge arrangement, $+2 \dots -4 \dots +2$, leads to a staggered crystal packing with a lattice energy dominated by large electrostatic terms.

Table 1: Visible Absorption Maxima of Some Cobalt Complexes

Complex	Nujol Mull	Solution
$[(\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OPO}_3)_2(\text{Mo}_2\text{O}_7)_2]$	508 ca 375 sh ^a	- -
$[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OPO}_3\text{H}]\text{ClO}_4 \cdot \text{aq}$	507 360	507 366
$[\text{Co}(\text{en})_2(\text{PO}_4)] \cdot \text{H}_2\text{O}$	525 370	529 377
$\text{cis}[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	490 ca 355 sh	492 359

^a sh, shoulder

Acknowledgments.- This research has been supported by the Office of Naval Research through Contract No. N00014-75-C-0945.

Figure Caption

Figure 1.- Infrared spectra, in KBr discs, of

(a) $[(\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OPO}_3)_2\text{Mo}_2\text{O}_{11}] \cdot 8\text{H}_2\text{O}$, and

(b) $\text{Na}_4[\text{P}_2\text{Mo}_2\text{O}_{11}] \cdot 13\text{H}_2\text{O}$

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Infrared Spectra of
(a), $[\text{Co}_2(\text{en})_4(\text{H}_2\text{O})_2(\text{PO}_4)_2(\text{MoO}_3)_5] \cdot 8\text{H}_2\text{O}$
(b), $\text{Na}_6[\text{P}_2\text{Mo}_5\text{O}_{23}] \cdot 13\text{H}_2\text{O}$

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Department of Chemistry Georgetown University Washington, D.C. 20057		2a. REPORT SECURITY CLASSIFICATION unclassified
		2b. GROUP
3. REPORT TITLE Pentamolybdo bis(cis-phosphatobisethylenediamineaquocobalt(III)). A 'Neutral' Heteropoly Complex.		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Rept.		
5. AUTHOR(S) (First name, middle initial, last name) Wonsuk Kwak and Michael T. Pope		
6. REPORT DATE November 1976	7a. TOTAL NO. OF PAGES 12	7b. NO. OF REFS 11
8a. CONTRACT OR GRANT NO. N00014-75-C-0945	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 5 14 TR-5	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Chemistry Branch Office of Naval Research Arlington, Va. 22217
13. ABSTRACT The synthesis, optical and infrared spectra of the title compound, $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OPO}_3]_2\text{Mo}_3\text{O}_{15}$ are described. The complex is an electrically neutral zwitterion.		

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